SYNTHESIS OF meso-ALDIMINOETIOPORPHYRIN

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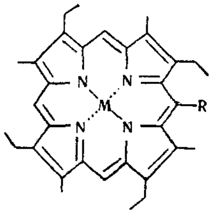
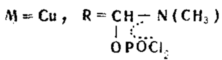
We have found that the reaction of phosphorus oxychloride, previously treated with a small amount of water, with (I), which is formed in the Vilsmeier reaction [1], gives intermediate porphyrin (II), the alkaline hydrolysis of which gives a formylporphyrin (III), whereas on treatment with concentrated ammonium hydroxide it gives an aldimine (IV) in 72% yield [spectrum in chloroform, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 408 (80.5), 508 (13.1), 540 (7.75), 577 (6.12), and 629 (3.68)]. Aldimine IV is extremely unstable in acidic media and is converted slowly and quantitatively to formylporphyrin III. Heating a solution of aldimine IV in chloroform in the presence of aqueous alkali for a long time does not result in appreciable formation of III.

Refluxing a solution of I in chloroform in the presence of ammonium hydroxide for 2-4 h gives a bright-red copper complex of aldimine V in 87% yield [spectrum in chloroform, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 407 (313), 534 (11.4), and 572 (16.07)], which is resistant to the action of both acids and bases. In acidic media, complex V exists in the nitrogen-protonated form (VI), and this leads to a sharp change in the electronic spectrum [λ_{max}, nm ($\varepsilon \cdot 10^{-3}$): 405 (61.0) shoulder, 448 (142), 608 (5.34), 650 (7.10) shoulder, and 710 (11.7)]. The formation of aldimine V is facilitated considerably if complex I is first treated with acetic or trifluoroacetic acid. When this is done, it is converted to a complex with a fixed meso-dimethylformaldimino group, as in the formation of intermediate porphyrin II, the reaction of which with ammonium hydroxide gives aldimine V in 89.5% yield in a few seconds.





$M = Cu$, $R = \underset{\substack{| \\ OPOCl_2}}{CH}-N(CH_3)_2$; II $M = 2H$, $R = CH=\overset{+}{N}(CH_3)_2Cl^-$; III $M = 2H$, $R = CHO$;

IV $M = 2H$, $R = CH=NH$; V $M = Cu$, $R = CH=NH$, VI $M = Cu$, $R = CH=\overset{+}{N}H_2$

The structures of IV and V were confirmed by the results of elementary analysis and the IR and mass spectra. The mass spectrum of aldimine IV is characterized by the presence of intense peaks with m/e 503, 505, and 507, which correspond to $(M-2)^+$, M^+, and $(M+2)^+$ ions, respectively. The most intense peak with m/e 564 in the mass spectrum of V corresponds to the $(M-2)^+$ ion, whereas a molecular ion peak is absent.

LITERATURE CITED

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